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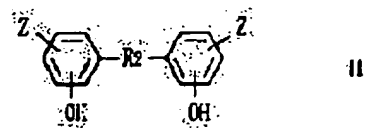
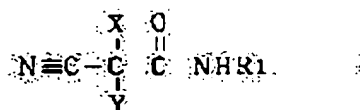
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(54) GERMICIDE AND STERILIZATION

(57)Abstract:

PURPOSE: To obtain a germicide capable of stabilizing a halocyanoacetamide compound, suppressing its decomposition due to sunlight and hydrolysis, free from skin irritation and excellent in stability and handleability.

CONSTITUTION: This germicide contains (A) a halocyanoacetamide compound, preferably a compound of formula I (X is a halogen; Y is a halogen or H, R1 is H or a lower alkyl), e.g. 2,2-dibromo-3-nitrylopropionic amide or its salt and (B) a bisphenol-based compound, preferably a compound of formula II (Z is H, a halogen or an alkyl; R2 is a direct bond or a spacer), e.g. 2,2-bis(4-hydroxyphenyl)propane. The component A is used in an amount of 0.1-3mol, especially 0.5-1.5mol based on 1mol of the component B. The formation of clathrate compound, e.g. clathrate compound of the component A with the component B obtained by



mixing both components is desirable. Further effect such as prevention of skin irritation in addition to stability is obtained by using the clathrate compound.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[The technical field to which invention belongs] this invention contains a halo cyanoacetamide compound, or the salt and a bisphenol system compound, and relates to the sterilization method using the germicide and it which are excellent in medicine stability.

[0002]

[Description of the Prior Art] Although use of a recycle water system is briskly performed with the increase in the need of industrial water, on the occasion of such use, control and suppression of multiplication of a microorganism are an important problem. Moreover, it is going over the calamity by multiplication of a microorganism, and the calamity by mold generating extensively with diversification of industrial materials besides these industrial use water. Measures to the slime problem by the microorganisms (a fungus, a bacteria, yeast, algae, etc.) which are parasitic on the service water in a paper manufacture process, industrial use cooling water or the lubricating oil for metalworking, a water emulsion, a swimming pool, etc., a microorganism calamity, etc. are especially taken pressing need. In order to prevent generating of these microorganisms or to remove recently, the halo cyanoacetamide compound which has the antibacterial action which had a latus antimicrobial spectrum, for example, was excellent to a bacterium, yeast, mold, etc. is used as a germicide. For example, in JP,61-83105,A, JP,62-70301,A, JP,3-176407,A, and JP,5-201810,A, it is 5-chloro. - The antimicrobial agent containing iso thiazolone compounds, such as 2-methyl-4-iso thiazoline-3-ON, and halo cyanoacetamide compounds, such as 2,2-dibromo-3-nitrilopropionamide, is indicated.

[0003] The aquosity tablet which contains an iso thiazolone compound, the aquosity solvent for dissolving this compound, and the 2,2-dibromo-3-nitrilopropionamide as a part for stable Chemicals in JP,4-9305,A is indicated.

[0004] Furthermore, it is in JP,60-231603,A. The antimicrobic agent which combined halo nitroglycerine alcohol and the cyanoacetamide compound is indicated, and it is 2-BUROMO-2-nitroglycerine in JP,2-42007,A. - 1 and 3-diacetoxy propane and 5-chloro - The industrial use germicide which combined the germicide chosen from iso thiazolone compounds, such as 2-methyl-4-iso thiazoline-3-ON, BUROMO nitroglycerine ethanol, and halo cyanoacetamide compounds (2,2-dibromo-3-nitrilopropionamide etc.) is indicated.

[0005] However, a halo cyanoacetamide compound has skin irritation and cautions on handling are required for it. Moreover, decomposing easily by hydrolysis by daylight or water etc. is known (5 journal OBUAGURIKARUCHARU- and the 21st volume of - hood chemistry, No. 1973). Therefore, the storage in the place where beams of light, such as daylight, and moisture exist is difficult, and it is difficult for disassembly of a halo cyanoacetamide compound to color, and for quality to deteriorate remarkably, and to offer the stable tablet. Moreover, poisonous cyano gas generates with disassembly of a halo cyanoacetamide compound. Therefore, on handling, it is very dangerous and to prevent generation of cyano gas is also made into pressing need.

[0006]

[Problem(s) to be Solved by the Invention] Therefore, the purpose of this invention is to offer the germicide which a halo cyanoacetamide compound or its salt stabilized. Although other purposes of this invention contain a halo cyanoacetamide compound or its salt, they are to offer the germicide which there is no skin irritation, stability and handling nature are high, continue at a long period of time, and can maintain the activity of a halo cyanoacetamide compound or its salt. The purpose of further others of this invention can suppress decomposition by daylight, hydrolysis, etc., and is to offer the germicide which does not generate poisonous gas etc.

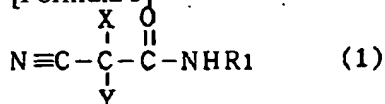
[0007]

[Means for Solving the Problem] In order to attain the aforementioned purpose, when this invention persons made the bisphenol compound live together with a halo cyanoacetamide compound or its salt wholeheartedly as a result of examination, they find out that a halo cyanoacetamide compound or its salt is stable, and came to complete this invention.

[0008] That is, the germicide of this invention contains (1) halo cyanoacetamide compound, or the salt and a bisphenol system compound. Setting to this germicide, (2) halo cyanoacetamide compound is a general formula (1).

[0009]

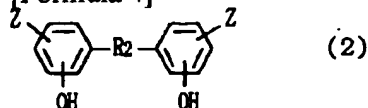
[Formula 3]



(-- as for a halogen atom or a hydrogen atom, and R₁, X shows a halogen atom among a formula, and Y shows a hydrogen atom or a low-grade alkyl group the compound expressed with) -- you may be -- (3) bisphenol system compound -- general formula (2)

[0010]

[Formula 4]



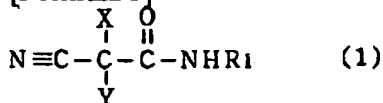
(-- the inside of a formula and Z are the same respectively -- or it differs, a hydrogen atom, a halogen atom, or an alkyl group is shown, and R₂ shows a joint hand or a spacer You may be the compound expressed with). (4) The aforementioned spacer R₂ You may be a low-grade alkylene machine or a sulfonyl machine. (5) 2,2-dibromo-3-nitrilopropionamide etc. is contained in the aforementioned halo cyanoacetamide compound, and screw (4-hydroxyphenyl) methane, 1, and 1-screw (4-hydroxyphenyl) ethane, 2, and 2-screw (4-hydroxyphenyl) propane, 4, and 4'-dihydroxy phenyl sulfone and 2, and 2'-dihydroxy -5, a 5'-dichlorophenyl sulfone, etc. are contained in (6) bisphenol system compound. The germicide of this invention may consist of clathrate compounds of a halo cyanoacetamide compound, or the salt and a bisphenol system compound. By the method of this invention, the aforementioned germicide is sterilized by adding to a processed liquid.

[0011]

[Embodiments of the Invention] The halo cyanoacetamide compound used by this invention is typically expressed with a general formula (1) etc.

[0012]

[Formula 5]



((X shows a halogen atom among a formula) As for Y, a halogen atom or a hydrogen atom, and R₁ show a hydrogen atom or a low-grade alkyl group) A fluorine, chlorine, a bromine, and a YOH atom are

contained in the halogen atom expressed with X and Y. A chlorine atom or a bromine atom, especially a bromine atom are contained in a desirable halogen atom. In the compound expressed with the aforementioned formula (1), the halo cyanoacetamide compound both X and whose Y are a halogen atom, especially a bromine atom is suitable.

[0013] R1 As a low-grade alkyl group, the about one to six carbon numbers [, such as a methyl group, an ethyl group n-propyl group, an iso-propyl group, n-butyl, an iso-butyl, a sec-butyl, a tert-butyl, a pentyl machine, and a hexyl machine,] shape of a straight chain and a branched chain-like low-grade alkyl group are mentioned, for example. desirable R1 **** -- a hydrogen atom or C1-4 alkyl group is contained, and especially a hydrogen atom, a methyl group, and an ethyl group are desirable it carries out -- having -- desirable R1 They are a hydrogen atom or a methyl group.

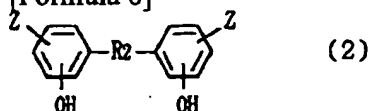
[0014] As an example of a halo cyanoacetamide compound (1) For example, 2-halo 3-nitrilopropionamide, such as 2-chloro-3-nitrilopropionamide and 2-BUROMO-3-nitrilopropionamide; 2 and 2-dichloro-3-nitrilopropionamide, 2, such as 2,2-dibromo-3-nitrilopropionamide and 2-chloro-2-BUROMO-3-nitrilopropionamide, 2-dihalo-3-nitrilopropionamide; N-methyl-2-chloro-3-nitrilopropionamide, N-C1-3 alkyl-2-halo 3-nitrilopropionamide, such as N-methyl-2-BUROMO-3-nitrilopropionamide; The N-methyl -2, 2-dichloro-3-nitrilopropionamide, One to N-C3 alkyls -2, such as N-methyl-2,2-dibromo-3-nitrilopropionamide, 2-dihalo-3-nitrilopropionamide, etc. are mentioned. These compounds are independent, or two or more sorts can use them, mixing. As a salt of a halo cyanoacetamide compound, organic acid chloride, such as inorganic-acid salts, such as a hydrochloride, hydrobromate, a sulfate, and a nitrate, acetate, a trichloroacetic-acid salt, a trifluoroacetic-acid salt, methanesulfon acid chloride, and a p-toluenesulfonic-acid salt, can be illustrated, for example.

[0015] 2 and 2-dichloro-3-nitrilopropionamide, 2,2-dibromo-3-nitrilopropionamide, N-methyl-2,2-dibromo-3-nitrilopropionamide, etc. are contained in a desirable halo cyanoacetamide compound. As a halo cyanoacetamide compound, 2,2-dibromo-3-nitrilopropionamide etc. is used in many cases.

[0016] The bisphenol system compound used for this invention is a general formula (2) typically.

[0017]

[Formula 6]



(the inside of a formula and Z are the same respectively -- or it differs, a hydrogen atom, a halogen atom, or an alkyl group is shown, and R2 shows a joint hand or a spacer) etc. -- it is expressed A fluorine, chlorine, a bromine, and an iodine atom are contained in the halogen atom expressed with Z. Desirable halogen atoms are a chlorine atom or a bromine atom, especially a chlorine atom. C1-6 alkyl groups, such as a methyl, ethyl, a propyl, an isopropyl, butyl, an isobutyl, s-butyl, t-butyl, a pentyl, and a hexyl machine, are contained in the alkyl group expressed with Z. C1-4 alkyl group especially a methyl group, or an ethyl group is contained in a desirable alkyl group. In addition, in the benzene ring of a bisphenol compound (2), the aromatic ring, for example, the benzene ring, the heterocycle, etc. may condense.

[0018] R2 As a spacer with which it is expressed, for example Alkylene machine for example, methylene, ethylene, propylene, 2, and 2-dimethyl methylene -- The shape of a straight chain, branched chain-like C1-10 alkylene machines, such as 2 and 2-dimethyl ethylene and tetramethylen, An alkenylene group, cyclo alkylene machines (for example, a vinylene machine, a pro PENIREN machine, etc.) For example, (1, 4-cyclo alkylene, 1, and 1-cyclo alkylene machine) etc., Sulfonyl machine-SO₂-, sulfinyl machine-SO-, sulfide machine-S-, An oxygen atom, oxo basis >CO, thioxo machine >SO, a malonyl machine, a succinyl machine, Saturated-fat group dicarbonyl machine-OCRCO-, such as a glutaryl machine and a horse mackerel POIRU machine (R shows an about one to ten-carbon number alkylene machine), Thiocarbonyl-group >CS, imino group >NH, and hydrazo machine-NH-NH-, azo-N=N-, ureylene machine-NHCONH-, etc. can be illustrated.

[0019] Spacer R2 As a compound (2) which is an alkylene machine For example, screw (4-

hydroxyphenyl) methane, screw (4-hydroxy-3-chlorophenyl) methane, Screw (4-hydroxy-3-methylphenyl) methane, a screw (4-hydroxyphenyl) phenylmethane, Screw (4-hydroxyphenyl) diphenylmethane, 1, and 1-screw (4-hydroxyphenyl) ethane, 1 and 1-screw (4-hydroxy-3-methylphenyl) ethane, 1, 1 and 2, 2-tetrakis (3-methyl-4-hydroxyphenyl) ethane, 1 and 1-screw (4-hydroxyphenyl) propane, 2, and 2-screw (4-hydroxyphenyl) propane, 2 and 2-screw (4-hydroxy-3-chlorophenyl) propane, 2, and 2-screw (4-hydroxy-3, 5-dichlorophenyl) propane, 2 and 2-screw (4-hydroxy-3-methylphenyl) propane, 2, and 2-screw (4-hydroxy-3-ethyl phenyl) propane, 2 and 2-screw (4-hydroxyphenyl) butane, 2, and 2-screw (4-hydroxyphenyl) pentane, 2 and 2-screw (4-hydroxyphenyl)-3-methyl butane, 2, and 2-screw (4-hydroxyphenyl) hexane, 2 and 2-screw (4-hydroxyphenyl)-4-methyl pentane, 1, and 1-screw (4-hydroxyphenyl)-1-phenyl ethane etc. can be illustrated.

[0020] Spacer R2 As a compound (2) which is an alkenylene group, 1, 1, 4, and 4-tetrapod (4-hydroxyphenyl)-2-butyne -1, 4-diol, 1, 1 and 6, 6-tetrapod (4-hydroxyphenyl) -2, 4-hexa gene -1, 6-diol, 4, and 4'-dihydroxy stilbene disulfonic acid etc. is mentioned, for example. Spacer R2 1 and 1-screw (4-hydroxyphenyl) cyclopentane, 1, and 1-screw (4-hydroxyphenyl) cyclohexane etc. is contained in the compound (2) which is a cyclo alkylene machine.

[0021] Spacer R2 To the compound (2) which is a sulfonyl machine For example, 4 and 4'-dihydroxy phenyl sulfone, 4, and 4'-dihydroxy -3, a 3'-dimethylphenyl sulfone, 2 and 2'-dihydroxy -5, 5'-dichlorophenyl sulfone, 4, and 4'-dihydroxy -3, a 3'-dichlorophenyl sulfone, etc. are contained. Spacer R2 As a compound (2) which is a sulfinyl machine, 4 and 4'-dihydroxy phenyl SURUFIN, screw (4-hydroxy-3-chlorophenyl) SURUFIN, etc. are mentioned, for example. Spacer R2 As a compound which is a sulfide machine, a 4 and 4'-dihydroxydiphenyl sulfide etc. is mentioned, for example.

[0022] R2 In the compound which is an oxygen atom, it is a 4 and 4'-dihydroxy diphenyl ether and R2. To the compound which is an oxo basis For example, a 4 and 4'-oxy-screw (6-t-butyl-3-methyl phenol), A 1 and 1'-oxy-screw (2-naphthol), 2, and 2-oxy-screw (4-methyl-6-t-butylphenol) etc. is mentioned, and it is R2. To the compound which is a thioxo machine For example, 4 and 4'-thio screw (6-t-butyl-3-methyl phenol), 1, and 1'-thio screw (2-naphthol), 2, and 2-thio screw (4-methyl-6-t-butylphenol) etc. is mentioned.

[0023] R2 JI (4-hydroxy benzoyl) methane [for example,], 1, 2-JI (4-hydroxy benzoyl) propane, 1, and 4-JI (4-hydroxy benzoyl) butane etc. is contained in the compound which are saturation aliphatic dicarbonyl machines, such as a malonyl machine, a succinyl machine, a glutaryl machine, and a horse mackerel POIRU machine. R2 In the compound which is a thiocarbonyl group, it is a 1 and 1'-screw (4-hydroxyphenyl thione) and R2. In the compound which is an imino group, it is for example, a JI (4-hydroxyphenyl) amine and R2. In the compound which is a hydrazo machine, it is a 4 and 4'-dihydroxy hydrazobenzene and R2. A 4 and 4'-dihydroxy azobenzene etc. is contained in the compound which is an azo machine. Furthermore, R2 An N' and N'-JI (4-hydroxyphenyl) urea etc. can be illustrated to the compound which is a ureylene machine. These compounds (2) are independent, or two or more sorts can use them, mixing.

[0024] a desirable compound (2) -- R2 compound [which is an alkylene machine (especially C1-3 alkylene machine) -- for example Screw (4-hydroxyphenyl) methane, 1, and 1-screw (4-hydroxyphenyl) ethane,], such as 2 and 2-screw (4-hydroxyphenyl) propane, 2, and 2-screw (4-hydroxy-3-chlorophenyl) propane, and R2 compound [which is a sulfonyl machine -- for example], such as 4 and 4'-dihydroxy phenyl sulfone, 2, and 2'-dihydroxy -5 and a 5'-dichlorophenyl sulfone, etc. is contained.

[0025] The germicide of this invention can be easily obtained by mixing a halo cyanoacetamide compound, or the salt and a bisphenol system compound at a suitable rate. The rate of a halo cyanoacetamide compound, or the salt and a bisphenol system compound can be chosen in the large range, unless stability is spoiled, and the 0.1-3 mols of the 0.25-2 mols of the amount of a halo cyanoacetamide compound or its salt used are about 0.5-1.5 mols still more preferably preferably to one mol of bisphenol system compounds.

[0026] Furthermore, in mixture of the aforementioned component, it is desirable to make the clathrate compound of a halo cyanoacetamide compound, or the salt and a bisphenol system compound, for example, a halo cyanoacetamide compound with a bisphenol system compound, and the clathrate

compound of the salt generate. In this case, in addition to stability, much more effect of being able to prevent a skin stimulus is acquired. a still higher effect is acquired -- being alike -- it is desirable that the inclusion of a halo cyanoacetamide compound or the 0.1-2 mols of the 0.25-1.5 mols of its salt is carried out in 0.5-1 mol still more preferably to one mol of bisphenol system compounds

[0027] A clathrate compound can be prepared as follows, for example. a bisphenol system compound -- receiving -- 0.5 - 50 weight twice -- desirable -- 0.5 - 30 weight section -- a halo cyanoacetamide compound or its salt, and a bisphenol system compound are dissolved using a twice [1 - 20 weight] as many solvent as this still more preferably Especially a melting temperature is not restricted but can be preferably dissolved at the temperature of about 40-60 degrees C 20-80 degrees C according to the kind of solvent. In this case, after dissolving a halo cyanoacetamide compound or its salt, and a bisphenol system compound in a solvent different, respectively, each solution may be mixed and each aforementioned compound may be dissolved in the same solvent. Thus, a medium (poor solvent) with refractory halo cyanoacetamide compound or its salt is added to the prepared mixed liquor, and a crystal is deposited. the range in which the amount of the aforementioned medium used does not spoil the deposit nature of a crystal -- it can choose -- for example, the aforementioned solvent -- receiving -- 0.1 - 50 weight twice -- it is about 0.5-20 weight twice preferably for depositing a crystal -- a medium (poor solvent) with refractory halo cyanoacetamide compound or its salt -- in addition -- for example, what is necessary is to be the time beyond 0.5 - 48 hours, or it, and just to leave it comparatively at low temperature (for example, temperature of -10 degrees C - about 25 degrees C) The crystal which deposited can be obtained by drying by reduced pressure drying etc. as a powdered clathrate compound of a halo cyanoacetamide compound, or the salt and a bisphenol system compound, after filtration etc. separates with a solution.

[0028] As a solvent (good solvent) in which a halo cyanoacetamide compound, or the salt and a bisphenol system compound is dissolved For example, a methanol, ethanol, n-propanol, iso-propanol, Alcoholic system solvents, such as a tert-butanol; Ethylene glycol, A diethylene glycol, a triethylene glycol, a propylene glycol, A dipropylene glycol, tripropylene glycol, 1, 4-butanediol, 1,5-pentanediol, an ethylene glycol monomethyl ether, Glycol system solvents, such as ethylene glycol monoethyl ether and tripropylene glycol monomethyl ether; An acetone, Ether system solvents, such as ketone system solvent; dioxanes, such as a methyl ethyl ketone and a methyl isobutyl ketone, a tetrahydrofuran, and ethyl ether; for example Ester system solvents, such as ethyl acetate, butyl acetate, and an isobutyl acetate; Benzene, Aromatic-hydrocarbon system solvents, such as toluene, a xylene, a methyl naphthalene, and solvent naphtha; A methylene chloride, Halogenated-hydrocarbon system solvents, such as a carbon tetrachloride and chloroform; polar solvents, such as a dimethylformamide, dimethyl sulfoxide, and an acetonitrile, etc. are mentioned. You may mix two or more kinds of these solvents.

[0029] Moreover, as a medium (poor solvent) with a refractory halo cyanoacetamide compound, aliphatic series or alicycle group hydrocarbons, such as water; n pentane, n-hexane, n-heptane, n-octane, n-nonane, a cyclohexane, cycloheptane, a cyclooctane, a cyclo nonane, and a liquid paraffin, etc. are mentioned, for example. These poor solvents are independent, or two or more sorts can use them, mixing. As a poor solvent to a halo cyanoacetamide compound, water is used in many cases.

[0030] Especially the gestalt of the germicide of this invention is not restricted, for example, although you may be powder material, a granule, a fines agent, a paste agent, etc., it is usually used in many cases as solution, such as an emulsion, water dispersible powder, water soluble powders, and suspension. as a solid support in powder material etc., clay, such as a kaolin, a bentonite, and acid clay, talc, silicas, an alumina, activated carbon, etc. mention, for example -- having -- these solid supports -- a kind -- or two or more sorts can be used As a solvent (liquid support) in solution, the various solvents which distribute [the dissolution or] the aforementioned component, for example, water, and an organic solvent can be used. As an organic solvent, for example Methyl alcohol, ethyl alcohol, Alcohols, such as isopropyl alcohol; Ester; acetones, such as methyl acetate and ethyl acetate, Ketones, such as a methyl ethyl ketone and a methyl isobutyl ketone; A dichloromethane, Halocarbon hydrogen, such as a dichloroethane, chloroform, and a carbon tetrachloride; A dioxane, Ether, such as a tetrahydrofuran; A

dimethylformamide, dimethyl sulfoxide, Polar solvents, such as an acetonitrile; Ethylene glycol, a diethylene glycol, Polyhydric alcohol, such as a polyethylene glycol, a propylene glycol, a dipropylene glycol, tripropylene glycol, a polypropylene glycol, 1, 4-butanediol, 1,5-pentanediol, and a glycerol, the derivative of those, etc. are mentioned. Carbitols, such as the cellosolves; diethylene-glycol monomethyl ether, such as a glycol system solvent, for example, a methyl cellosolve, ethyl SERORUBU, and a butyl cellosolve, and a diethylene glycol monoethyl ether, are contained in the derivative of polyhydric alcohol. these solvents -- a kind -- or two or more sorts can use it, mixing

[0031] Although the amount of the total used of the aforementioned compound (1) and (2) changes with a pharmaceutical form and the purpose of use, uses, etc., generally, it can be chosen from 0.1 - 99.9% of the weight of the range among a tablet, and, specifically, can be chosen from about 10 - 99.9% of the weight of the range by powder material about 10 to 80% of the weight by water dispersible powder about 0.1 to 20% of the weight at a solution agent.

[0032] Furthermore, to the germicide and clathrate compound of this invention, you may add assistants, such as well-known various additives, for example, other germicides, a surfactant, an antioxidant, stabilizers (a carboxymethyl cellulose, an alginic acid, its salt, polyvinyl alcohol, etc.), and a rust-proofer, perfume, etc. in the purpose, a use, etc. as this germicide -- an iso thiazoline system compound (ON for example, 1 and 2-Benz iso thiazoline-3-) 2-methyl-4-iso thiazoline-3-ON, 5-chloro - 2-methyl-4-iso thiazoline-3-ON, 5-BUROMO - 2-methyl-4-iso thiazoline-3-ON and 2-ethyl-4-iso thiazoline-3-ON, 5-chloro - 2-ethyl-4-iso thiazoline-3-ON and 2-propyl-4-iso thiazoline-3-ON, 2-octyl-4-iso thiazoline-3-ON, 5-chloro - 2-octyl-4-iso thiazoline-3-ON, 4, 5-dichloro - 2-octyl-4-iso thiazoline-3-ON etc., a KABA mate system compound (for example, a 3-iodine-2-propynyl butyl KABA mate --) Alcoholic system compounds, such as a methyl-2-Benz imidazole KABA mate for example, 2 and 2-dibromo-2-nitroglycerine ethanol, 2, and 2-dichloro-2-nitroglycerine ethanol -- Dithiols system compounds (for example, 4, 5-dichloro -1, 2-dithiol-3-ON, etc.), such as 2-BUROMO-2-chloro-2-nitroglycerine ethanol, 2-BUROMO-2-nitropropane -1, and 3-diol, etc. are mentioned. You may use together two or more kinds of these germicides. especially the amount of these germicides used restricts -- not having -- for example, the total amount 100 weight section of a halo cyanoacetamide compound and a bisphenol system compound -- receiving -- the 0 - 200 weight section -- it can choose from the range about the 0 - 100 weight section preferably

[0033] As a surfactant, any of well-known surfactants, such as soap, a Nonion system surfactant, an anion system surfactant, a cation system surfactant, both ion surfactant, and a high molecular surface active agent, are sufficient. A Nonion system surfactant and an anion system surfactant are preferably used among these surfactants. As for a metaphor, the polyoxyalkylene alkylphenyl ether (polyoxyethylene nonylphenyl ether etc.), an ethyleneoxide, a propylene-oxide block copolymer, etc. are mentioned to a Nonion system surfactant. As an anion system surfactant, an alkylbenzene sulfonic-acid metal salt, an alkyl naphthalene sulfonic-acid metal salt, a polycarboxylic-acid type surfactant, a dialkyl sulfo succinic-acid ester metal salt, polyoxyethylene distyrenated phenyl ether sulfate ammonium salt, a ligninsulfonic-acid metal salt, etc. are mentioned, and sodium salt, potassium salt, etc. are mentioned as a metal salt.

[0034] As an antioxidant, amine system antioxidants, such as phenol system antioxidants [, such as a 2 6-G t-butyl-4-methyl phenol, 2 and 2'-methylene screw [4-methyl-6-t-butylphenol],], alkyl diphenylamine, N, and N'-G s-butyl-p-phenylene diamine, etc. are mentioned. Generally additives, such as these surfactants and an antioxidant, can be used to the tablet whole quantity at a rate about 0 - 80 % of the weight (for example, 5 - 80 % of the weight). After adding in case a halo cyanoacetamide compound and a bisphenol system compound are mixed, and mixing, you may add these additives in the case of tablet-izing.

[0035] Thus, while the germicide of the obtained this invention does not have skin irritation and having the outstanding antibacterial action, the high germicidal action continued and stabilized at the long period of time is shown. Therefore, it is useful, when adding to various processed liquids and making high antibacterial and sterilization activity discover. Specifically, while being able to use as the slime control agent and sterilization cleaning agent of a paper manufacture pulp mill and a cooling-water-flow

process, it can be used as industrial use germicides, such as antiseptics of metal working fluid, casein, starch coating liquid, a water paint, and water adhesives.

[0036] When using for a paper manufacture process, it is desirable to add a germicide in the place where pulp exists by the shape of a slurry, for example, comparatively low RIFURA of a pulp density, a flow box, the Hakusui pit, etc. Moreover, to a synthetic-resin emulsion, a starch paste, glue, and cutting oil, a germicide may be added directly, or a germicide may be added to the coating color which is the secondary product, a paint, printing ink, adhesives, a sizing compound, etc. Moreover, it can use for sterilization processing of a makeup supply, a nonwoven fabric, leather, etc.

[0037] Since high sterilization and high antimicrobial activity are discovered even if little, the germicide of this invention does not have a bad influence on the property of a processed liquid, for example, distributed stability, a fluidity, etc. Moreover, since stability is high, it continues at a long period of time, and high sterilization and high antimicrobial activity can be maintained. Therefore, corresponding to the kind of processed liquid, the addition of a germicide is converted into a halo cyanoacetamide compound, and can be chosen 1-750 ppm preferably 0.1-10000 ppm suitably [it is still more desirable and] from the range of about 5-500 ppm. The addition of a germicide is converted into a halo cyanoacetamide compound. In the case of paper manufacture industrial water, the duty of water is received. For example, 0.01-200 ppm, About 0.1-100 ppm and a synthetic-resin emulsion are received preferably. 1-1000 ppm, 1-1000 ppm 1-1000 ppm are about 10-200 ppm to the coating color using about 10-500 ppm and a starch paste as a binder to about 10-500 ppm and a surface-size agent preferably.

[0038]

[Effect of the Invention] Since the germicide of this invention is combined with the bisphenol system compound, it can stabilize a halo cyanoacetamide compound or its salt. Moreover, in spite of including a halo cyanoacetamide compound or its salt, there is no skin irritation, and stability and handling nature are high, continue at a long period of time, and can maintain the high activity of a halo cyanoacetamide compound. Furthermore, decomposition by daylight, hydrolysis, etc. can be suppressed, poisonous gas etc. does not generate, and it can be effectively used as a germicide.

[0039]

[Example] this invention is not limited by these examples although this invention is explained more below at a detail based on an example.

Chloroform 1ml was added to example 12 and 2-screw (4-hydroxyphenyl) propane 1g, and it heated and dissolved in 50 degrees C. 2,2-dibromo-3-nitrilopropionamide 1.06g melted to methanol 1ml was added to this solution. It returned to the room temperature, n-hexane 8ml was added, and it was left in the refrigerator on the 1st. Reduced pressure drying of the generated crystal was carried out after suction filtration, and 1.6g of powdered white crystals was obtained. Even if it dealt with the obtained white crystal empty-handed, there was no stimulus to the skin. When the fixed quantity of the content of the halo cyanoacetamide under this powder crystal was carried out by liquid chromatography, content was 51.6 % of the weight. Moreover, it checked that the aforementioned product was a clathrate compound by powder X-ray analysis and the infrared absorption spectrum.

The peak spacing of the powder X-ray data of a clathrate compound (angstrom); 14.866 (1/1 0; 100), 4.453 (1/1 0; 43), 2.866 (1/1 0; 21), 3.501 (1/1 0; 20)

Methanol 4ml was added to infrared-spectrum IR(cm-1); 1710.0, 1376.9, 1510.0, 3365.2 example 22, and 2-screw (4-hydroxyphenyl) propane 1g and 2,2-dibromo-3-nitrilopropionamide 1g of a clathrate compound, and it heated and dissolved in 50 degrees C. 9ml of water was added to this solution, and it was left in the refrigerator on the 1st. Reduced pressure drying of the produced crystal was carried out after suction filtration, and 1.9g of powdered white crystals was obtained. Even if it dealt with the obtained white crystal empty-handed, there was no stimulus to the skin. When the fixed quantity of the content of the halo cyanoacetamide in this powder was carried out in liquid chromatography, content was 50.7 % of the weight.

[0040] Methanol 4ml was added to example 34 and 4'-dihydroxy phenyl sulfone 1g and 2,2-dibromo-3-nitrilopropionamide 1g, and it heated and dissolved in 50 degrees C. 10ml of water was added to this solution, and it was left in the refrigerator on the 1st. When reduced pressure drying of the produced

crystal was carried out after suction filtration, 1.8g of powdered white crystals was obtained. Even if it dealt with the obtained white crystal empty-handed; there was no stimulus to the skin. When the fixed quantity of the content of the halo cyanoacetamide in this powder was carried out in liquid chromatography, content was 49.2 % of the weight.

[0041] Methanol 4ml was added to example 42, 2'-dihydroxy -5, and 5'-dichlorophenyl sulfone 1g and 2,2-dibromo-3-nitrilopropionamide 1g, and it heated and dissolved in 50 degrees C. 9ml of water was added to this solution, and it was left in the refrigerator on the 1st. Reduced pressure drying of the produced crystal was carried out after suction filtration, and 1.9g of powdered white crystals was obtained. Even if it dealt with the obtained white crystal empty-handed, there was no stimulus to the skin. When the fixed quantity of the content of the halo cyanoacetamide in this powder was carried out in liquid chromatography, content was 42.1 % of the weight.

[0042] The example 1 (weathering test) of an examination

2,2-dibromo-3-nitrilopropionamide of 1g of each was put into the plastic bag, respectively as the white crystal prepared in the example 1, and an example of comparison, and it was left for about 300 hours under the conditions (the humidity of 90%, temperature of 60 degrees C, and ultraviolet line intensity 2.8 w/m²) of a weathering test. Although the white crystal prepared in the example 1 300 hours after maintained white and change was not accepted, the 2,2-dibromo-3-nitrilopropionamide of the example of comparison was colored light yellow.

[0043] The example 2 (antimicrobial-activity measurement) of an examination

The multiple dilution method using the glucose agar medium was used, and bacteria, with mold and yeast, it cultivated for 28 degree-Cx three days, and asked for the minimum growth prevention concentration (Media Interface Connector and mug/ml) for 33 degree-Cx 18 hours.

[0044] The solution which dissolved 2,2-dibromo-3-nitrilopropionamide in water as an example of comparison was used using the germicide prepared in the example 1 as a sample. In addition, the sample was prepared so that the amount of both 2,2-dibromo-3-nitrilopropionamide might become the same in an examination. A sample offering bacillus and a measurement result are shown in Table 1.

[0045]

[Table 1]

表 1

供 試 菌	抗菌力MIC (μg/ml)	
	実施例 1	比較例
1) バチリス ズブチリス (<i>Bacillus subtilis</i>)	39. 2	39. 2
2) スタフィロコッカス アウレウス (<i>Staphylococcus aureus</i>)	78. 5	78. 5
3) エシェリキア コリー (<i>Escherichia coli</i>)	78. 5	78. 5
4) シュウドモナス エルギノサ (<i>Pseudomonas aeruginosa</i>)	39. 2	39. 2
5) セラチア マルセッセンス (<i>Serratia marcescens</i>)	78. 5	78. 5
6) アスペルギルス ニガー (<i>Aspergillus niger</i>)	>157	>157
7) ペニシリウム シトリナム (<i>Penicillium citrinum</i>)	>157	>157
8) クラドスポリウム クラドスポリオイデス (<i>Cladosporium cladosporioides</i>)	>157	>157
9) ムコール スピネッセンス (<i>Mucor spinescens</i>)	>157	>157
10) ロドトルラ ルブラ (<i>Rhodotorula rubra</i>)	>157	>157
11) サッカロミセス セレビスシアエ (<i>Saccharomyces cerevisiae</i>)	>157	>157

In an example 1 and the example of comparison, it is same to antimicrobial activity and Table 1 shows that antimicrobial activity is the same irrespective of the existence of an inclusion.

[0046] As 500g (clathrate compound) of germicides prepared in the example of examination 3 example 1, and the example of comparison. After putting 2,2-dibromo-3-nitrilopropionamide 500g into the desiccator (capacity 3.8L) and leaving it for three days at 60 degrees C, by observing discoloration of an indicator tube using a Kitagawa style extraction machine, the fixed quantity of the generated hydrogen cyanide was carried out, and it was converted into the amount of generation of the hydrogen cyanide per 1kg of samples (mg). A result is shown in Table 2.

[0047]

[Table 2]

表 2

	シアン化水素生成量 (mg/kg)
比較例	550
実施例 1	2.6

From Table 2, generating of cyano gas can be sharply reduced by processing with a bisphenol system compound and considering as a clathrate compound so that clearly.

[Translation done.]

* NOTICES *

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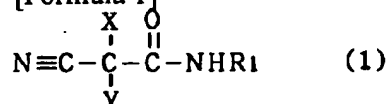
CLAIMS

[Claim(s)]

[Claim 1] The germicide containing a halo cyanoacetamide compound, or the salt and a bisphenol system compound.

[Claim 2] A halo cyanoacetamide compound is a general formula (1).

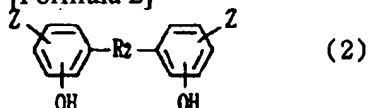
[Formula 1]



(-- X shows a halogen atom among a formula and, as for a halogen atom or a hydrogen atom, and R₁, Y shows a hydrogen atom or a low-grade alkyl group Germicide according to claim 1 which is the compound expressed with).

[Claim 3] A bisphenol system compound is a general formula (2).

[Formula 2]



(-- the inside of a formula and Z are the same respectively -- or it differs, a hydrogen atom, a halogen atom, or an alkyl group is shown, and R₂ shows a joint hand or a spacer Germicide according to claim 1 which is the compound expressed with).

[Claim 4] The germicide according to claim 3 whose spacer is a low-grade alkylene machine or a sulfonyl machine.

[Claim 5] The germicide according to claim 1 whose halo cyanoacetamide compound is 2,2-dibromo-3-nitrilopropionamide.

[Claim 6] The germicide according to claim 1 with which the bisphenol system compound was chosen from screw (4-hydroxyphenyl) methane, 1, and 1-screw (4-hydroxyphenyl) ethane, 2, and 2-screw (4-hydroxyphenyl) propane, 4, and 4'-dihydroxy phenyl sulfone and 2, and 2'-dihydroxy -5 and the 5'-dichlorophenyl sulfone and which is a kind at least.

[Claim 7] The germicide which consisted of clathrate compounds of a halo cyanoacetamide compound, or the salt and a bisphenol system compound.

[Claim 8] The sterilization method which adds a germicide according to claim 1 or 7 to a processed liquid.

[Translation done.]